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One-pot microwave-assisted approach of polydiacetylene/zinc oxide nanocomposite for reversible thermochromic

Chanita KHANANTONG[1,*], Thanutpon SRINOPKUN[1,*], Thitirut BOONMAK[1], and Jintana SIRIBOON[2]

[1] *Chemistry Program, Faculty of Science and Technology, Nakhon Sawan Rajabhat University, Nakhon Sawan, 60000, Thailand*
[2] *Laboratory of Advanced Polymer and Nanomaterials, School of Materials Science and Innovation, Faculty of Science, Mahidol University at Salaya, Phuttamonthon 4 Road, Nakorn Pathom, 73170, Thailand*

***Corresponding author e-mail**: chanita.k@nsru.ac.th, Thanutpon.p@nsru.ac.th

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Abstract

This study introduces a new technique to fabricate the reversible poly(PCDA/ZnO) nanocomposites thermochromism. Our preparation process is the solution-mixing method, which is supported by microwave synthesis time instead of ultrasonic bath or stirrer. The presence of ethanol molecules in aqueous media in the solution-mixing method induces dipolar polarization. In addition, the presence of Zn^{2+} leaking out of the ZnO can produce ionic polarization. These factors affect the shape of poly(PCDA/ZnO) nanocomposites based on their thermochromic properties. The optical properties of poly(PCDA/ZnO) nanocomposite were determined through UV-Vis absorption spectroscopy. The morphology of this nanocomposite was examined by scanning electron microscopy, and its crystallinity was investigated by X-ray diffraction. The inter-intrachain interaction was confirmed by infrared spectroscopy. In addition, the poly(PCDA/ZnO) nanocomposite embedding PVA was prepared. The reversible theromochromic properties of poly(PCDA/ZnO) nanocomposites demonstrated a higher color transition temperature with increasing microwave synthesis time. It is an important observation to understand the effect of microwave synthesis time on the morphology and reversible thermochromism of the poly(PCDA/ZnO) nanocomposite

1. Introduction

Polydiacetylene (PDA) is an established class of mechanochromic polymers that had previously been considered for use as colorimetric sensors [1-11]. The 10,12-pentacosadiynoic acid (PCDA) is a common diacetylene monomer that can form PDA self-assembly under an aqueous medium. Irradiating PDA self-assembly with ultraviolet light, X-rays, or -radiation induces photopolymerization, producing a conjugated-polydiacetylene with an ene-yne alternating backbone. [12-17]. This polymer conversion is a change from colorless to blue. The disruption of PDA structure by external stimuli such as heat, solvents, ions, etc. results in a stable color transition [10,18-20]. In some cases, the reversible color transition property such as thermochromics, is required due to reuse in green chemistry. Therefore, the modification of the PDA structure to produce a strong interaction between head groups has been investigated. The incorporation of metal oxide into PDA assemblies can produce a reversible color transition. For example, PDA/ZnO nanocomposite reveals reversible thermochromic behavior because the ZnO promotes strong interaction between headgroups [2,9,21-26]. Thus, this nanocomposite can be applied to detect various stimuli, for example, to detect heat for thermochromic sensor, to detect lactic acid for milk quality monitoring and to detect organic solvent for a health risk [2,9,24,25].

Generally, three PDA assembly synthesis methods are well-known. One of these pathways is the thin-film hydration method (TFHM). The diacetylene monomer was purified by an organic solvent evaporation step to form a thin film and then dispersed in an aqueous medium as described in previous works. [2,22,26]. This method spent a long time and involved multiple multi-steps in the process, resulting in a low yield of PDA assemblies and significant large aggregates caused by the agglomeration from uncomplete dispersion. To reduce the synthesis method step or consuming-time, the solution injection method (SIM) was demonstrated to synthesize PDA assemblies. The purified DA solution was directly injected into the aqueous medium. To remove the organic solvent, it was removed by ultrasonication or evaporation at a raised temperature and the aqueous suspension was incubated at cooling state, similar to the process used in the thin film method. [27-29]. During the SIM process, it requires some time for the solvent to be removed. Furthermore, these processes may not be suitable for large-scale production. Recently, the solution mixing method (SMM) was promoted for the fabrication of PDA/ZnO nanocomposites in ethanol-aqueous media. This method is very simple due to all the reagents were mixed in a solution phase while stirring at room temperature. The resultant PDA/ZnO nanocomposite via SMM demonstrated a smaller particle size than TFHM, but the morphology exhibited round-shape particles in both systems. The presence of an ethanol molecule in SMM might interrupt the layer packing of PDA/ZnO, inducing a thin PDA/Zn^{2+} layer [30]. However, the material designs, synthetic developments, and morphologically controlled nanostructures would be investigated to enhance PDA nanocomposite properties.

Microwave-assisted synthesis is widely explored in the processes of fabrication of various materials such as metal oxide nanoparticles [31,32] and organic synthesis [33,34]. The important role of microwave-assisted synthesis is the dramatic reduction of the processing time due to the high heating rate. The fast transfer of heating energy through radiation is more than convection. Moreover, the microwave-assisted method allows one to increase yields, decrease energy and reagent consumption, and chemical waste [35-37]. The nanoparticle was synthesized by the microwave-assisted method, resulting in coincidently uniform particle size, and a higher degree of crystallization [32,38]. The possible factor of microwave irradiation is a dielectric polarization. This factor relates to the material consisting of several phases which cause variables microwave radiation absorption coefficients. Water, alcohols, and other polar compound, mostly oxygen-containing compounds can readily absorb microwaves and convert their energy into heat. [35-39]. In addition, the previous study about PDA/ZnO nanocomposite demonstrated the occurrence of Zn^{2+} in nanocomposite leaking from ZnO, producing the intercalated PDA/Zn^{2+} structure [23]. The presence of Zn^{2+} may relate to the ionic polarization that responses to microwave heat. Therefore, the PDA/ZnO nanocomposite via SMM-microwave irradiation with ethanol-water as medium and Zn^{2+} may produce an efficient interaction between the polar and ionic entities of the reaction material. It may result in the exhibiting of different morphologies of PDA/ZnO nanocomposite. There is no report about the fabrication of PDA nanocomposite with SMM using microwave-assisted synthesis. Therefore, it is interesting in this study that we demonstrated a facile method to fabricate PCDA/ZnO nanocomposite via SMM with microwave-assisted synthesis. The different microwave durations affected different shapes, resulting in an interesting thermochromic property.

2. Experimental

2.1 Chemical reagents

The diacetylene monomer, 10,12-pentacosadiynoic acid (PCDA) ≥ 97.0% was commercially available at Sigma-Aldrich, USA. Ethanol (C_2H_3OH) 95% and polyvinyl alcohol (PVA) were purchased from Labscan, Thailand. Zinc oxide (ZnO) nanoparticles with diameter in the range of 20 nm to 200 nm were purchased from Nano Materials Technology (Thailand). Deionized water was used in the all experiments.

2.2 Preparation of poly(PCDA/ZnO) nanocomposite

For the synthesis poly(PCDA/ZnO) nanocomposite via solution mixing and microwave-assisted way using Microwave digestion ETHOS EASY SR-12 synthesizer, 0.038 g of PCDA monomer was dissolved in 5 mL 95% ethanol, and was sonicated in an ultrasonic bath ~5 min. Then, the solution was filtrated by 0.45 μm nylon filter to remove the polymerized polymer and was kept for the next step. The 0.019 g of ZnO was dissolved in deionized water and was sonicated by ultrasonic bath for 5 min. After that, 9.80 mL deionized water, 250 μL PDA monomer solution and 202 μL of ZnO to obtain 0.5 mM poly(PCDA/ZnO) with 10 wt% of the ZnO/DA ratio in all experiments as evaluated by previous work [2,22] . The suspension was added into a clean microwave vessel before heated by microwave irradiation with a power of 1000 W for 5, 15, 30 and 60 min. Afterwards, the suspension of PDA/ZnO was kept at 4°C and polymerized by using UV irradiation at the wavelength 254 nm for 5 min. For the poly(PCDA/ZnO) PVA film, the poly(PCDA/ZnO) nanocomposite solution was mixed with 10%w/v of polyvinyl alcohol (PVA) with ratio of 1:1 v/v. To form a flexible film, the mixture was poured into the clean cubic plastic plate and allowed to dry at room temperature.

2.3 Poly(PCDA/ZnO) nanocomposite characterization and thermochromism study

The morphology of synthesized poly(PCDA/ZnO) nanocomposite was examined by scanning electron microscope (SEM: JSM 7800F, JEOL operating at 5 kV). The interaction of poly(PCDA/ZnO) nanocomposite was characterized using Fourier-transformed infrared spectrometer (FT-IR, Thermo Scientific Nicolet 6700) using attenuated total reflectance mode (ATR). The crystalline structure and thermochromic property were studied using X-ray diffractometry (Bruker AXS Model D8 Discover λ(Cu-Kα) = 1.54 Å X-ray diffractometer) and UV-visible spectrometry (UV-Vis spectrophotometer, Evolution 201, Thermo Fisher Scientific), respectively. For the thermochromic investigation, all PDA/ZnO nanocomposite samples were equipped with a temperature-control unit. The calculation of %B and %R was modified based on the research conducted by M. Weston *et al.* [40].

3. Result and discussion

Morphologies of the poly(PCDA/ZnO) prepared by microwave-assisted technique with microwave synthesis times of 5, 15, 30 and 60 min are illustrated in Figure 1. The SEM images of poly(PCDA/ZnO) with a microwave synthesis time of 5 min exhibit an agglomerated form of hexagonal sheets. When the microwave synthesis time was increased to 15 min, it gave a clear morphology and larger particles were detected. At the microwave synthesis time of 30 min and 60 min, it was found that the particles had a more pronounced morphology and a relatively consistent size. Poly(PCDA/ZnO) structures with well-defined structures revealed high molecular ordering within the assemblies [41,42]. However, altering the ZnO/Da ratio may not impact the shape of the core-shell nanocomposite. Due to its wide particle size distribution, ZnO is incorporated into the center cavity of poly(PCDA). In agreement with Nisanart *et al.*, the variation in ZnO/DA ratio has hardly affected the size distribution. We observed that as the microwave synthesis time increased, the particle size also increased. The average particle sizes were approximately 100, 200, 300 and 400 nm after -microwave synthesis time by 5, 15, 30 and 60 min, respectively. Thermal gradients in the reaction solution were reduced through the synthetic process using microwave-assisted technique, which gave the reaction mixture a homogenous heating. This phenomenon resulted in a reliable nucleation and growth environment [43]. Furthermore, the mixed ethanol remained in the system of SMM has polar solvent properties. Dielectric loss in ethanol reacts to mechanical vibration (MV), producing heat within the molecules. Additionally, there is also an ionic polarization force from Zn^{2+} that comes from ZnO, giving the PDA more energy and supporting better alignment. As expected, they are more ordered compared to previously, resulting in the formation of nanomaterials with uniform size distribution [23,30,39].

The packing structure of poly(PCDA) and poly(PCDA/ZnO) was explored by XRD (Figure 2). The poly(PCDA) synthesized using a microwave synthesis time of 5 min in solid state form exhibited a bilayer lamellar structure consist of diffraction peaks at $2\theta = 1.80°$ (001), 5.18° (003) and 8.53° (005) which d-spacing of 4.7 nm. The XRD data revealed the absence of (002) and (004) diffraction planes, suggesting lower molecular ordering in poly(PCDA) system as discussed in previous study [8]. The detected XRD patterns of poly(PCDA/ZnO) at various microwave synthesis times had more diffraction peaks. This result suggests that the presence of ZnO promoting molecular ordering within the nanocomposites-significantly improved compared to the systems of poly(PCDA). The XRD patterns of the microwave synthesis time of 5 min constituted a set of peaks at $2\theta = 1.66°$ (001), 3.28° (002), 4.89° (003), 6.53° (004) and 8.15° (005). The bilayer d-spacing calculated from the first diffraction peak of poly(PCDA/ZnO) was 5.29 nm. The increase of d-spacing indicated the incorporation of Zn^{2+} at the carboxylic head groups of PDAs [23]. However, the microwave synthesis time, which was increased to 15, 30 and 60 min showed d-spacing at 5.36, 5.45 and 5.50 nm, respectively. The increased bilayer d-spacing synthesized via microwave demonstrated that the presence of strong interfacial interaction between the PDA head groups and the ZnO surface facilitated the molecular arrangement during the self-assembling process. Longer microwave synthesis time increased the heating energy, resulting in more relaxation time for the side chains and a high molecular arrangement within the assemblies. Therefore, the synthesis of nanocomposite via microwave increased local molecular ordering. The increase in bilayer d-spacing corresponded to the well-defined structures morphologies and larger particle size [39,43].

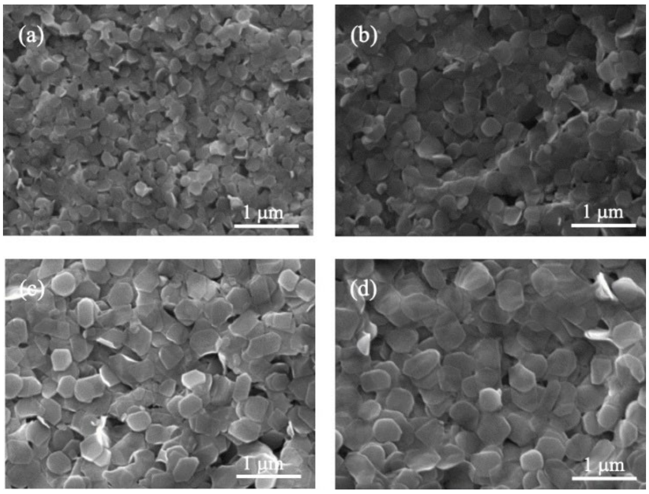

Figure 1. SEM images of poly(PCDA/ZnO) prepared by microwave-assisted technique with microwave exposure time. (a) 5 min, (b) 15 min, (c) 30 min, and (d) 60 min.

Microwave-assisted synthesis significantly decreases synthesis time while also providing low energy consumption with no impact in product yield [44]. The optical properties of poly(PCDA) and poly(PCDA/ZnO) solutions are shown in Figure 3. The absorption spectrum of poly(PCDA) assemblies exhibits a peak at 630 nm with broad shoulder at 585 nm. The spectrum of poly(PCDA/ZnO) exhibits λ_{max} at 644 nm with a broad vibronic shoulder at 592 nm. The spectra of poly(PCDA/ZnO) show slightly shift and sharper patterns compared to the poly(PCDA). This result suggests that the increase in molecular ordering of PDA chains corresponding to the more of interfacial interactions. An additional in system of poly(PCDA/ZnO) also observed low-energy band at 674 nm which is not found in poly(PCDA). This is due to the presence of PDA chain with a particularly long conjugation length in the poly(PCDA/ZnO) nanocomposites [22,45]. Additionally, we found that when microwave synthesis time increased absorption at 674 nm was enlarged. This finding indicated that the increase in synthesis time resulted in longer conjugation length in the nanocomposites according to the large particle size (see Figure 1).

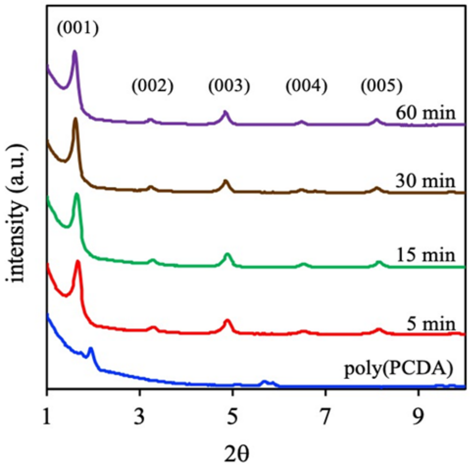

Figure 2. XRD patterns of poly(PCDA) with a microwave synthesis time of 5 min and poly(PCDA/ZnO) with various microwave exposure time.

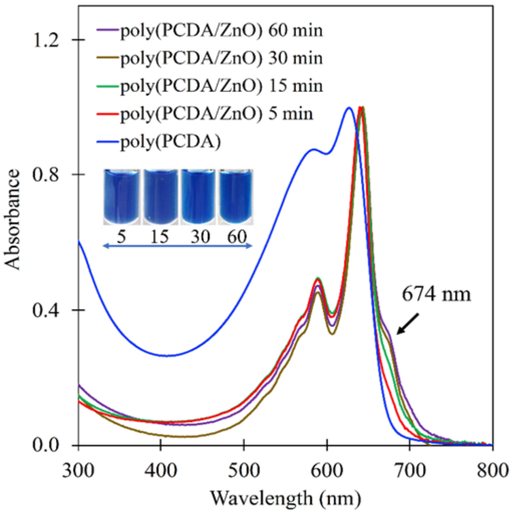

Figure 3. Absorption spectra of poly(PCDA) and poly(PCDA/ZnO). Photographs of poly(PCDA/ZnO) at different microwave synthesis time (inset).

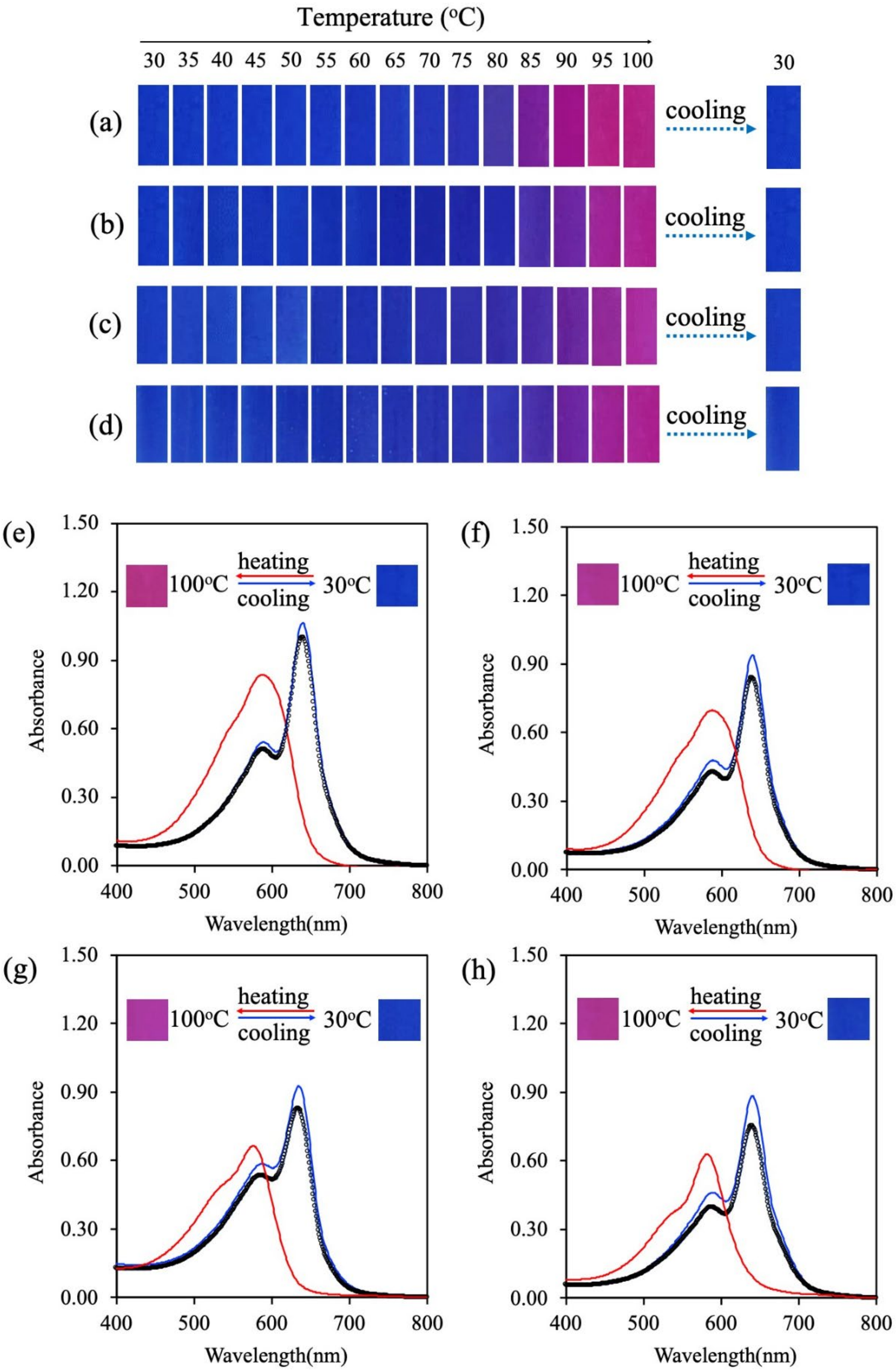

Figure 4. Color photographs and absorption spectra of poly(PCDA/ZnO) in aqueous suspension prepared by microwave-assisted technique with a microwave exposure time of (a, e) 5, (b, f) 15, (c, g) 30, and (d, h) 60 min evaluated during the process of heating and cooling.

The synthesis of poly(PCDA/ZnO) via microwave increases local molecular ordering resulting in the thermochromic behavior of poly(PCDA/ZnO) changing colors at high temperature. In the solution system, the color photographs are shown in Figure 4(a-d). The blue phase of poly(PCDA/ZnO) display λ_{max} at 640 nm and shoulder at 585 nm as shown in Figure 4(e-h). The increase of temperature above 90°C, the absorption spectra shifts to 585 nm, corresponding to the color transition from blue to magenta. To compare the color transition behaviors in more detail, the %color is plotted as a function of temperature, as shown in Figure 5. It is shown that the color transition from blue to magenta of the poly(PCDA/ZnO) with a microwave synthesis time of 5 min was detected at 90°C. The magenta color completely reverses to a blue color upon cooling to room temperature. The absorption spectra examined upon cooling observes similar pattern as before heating. The change in microwave synthesis time to 15, 30 and 60 min induces the color transition at 95°C which is about 5°C higher than the microwave synthesis time of 5 min. The findings suggest that as the microwave synthesis time is increased, the inter- and intrachain interactions within PCDA/ZnO become stronger. The size of PDA assemblies influences their sensitivity to external stimuli [41,42]. Our SEM study detected a much larger size of poly(PCDA/ZnO) in the microwave synthesis time of 5 min compared to the microwave synthesis time of 60 min (see Figure 1). We believed that the increase in particle size played a key role in the increase in color-transition temperature. The color transition temperature could be influenced by the change in molecular packing identified by XRD.

In the PDA/PVA film system, the poly(PCDA/ZnO) was mixed with the PVA solution by drop-casting on a glass slide. The film had a thickness of about 0.17 mm. It was annealed for 5 min at temperatures ranging from 50°C to 210°C while photographs were recorded (Figure 6(a-d)). The blue phase of poly(PCDA/ZnO) embed PVA film exhibit λ_{max} at 640 nm and shoulder at 590 nm as shown in Figure 6(e-h). In order to investigate the color reversibility, the film was allowed to cool down at room temperature. We observed that poly(PCDA/ZnO) in microwave synthesis time of 5 min exhibited the first color transition (blue to magenta) at ~110°C. The magenta color completely changed to a blue color when it cooled down to room temperature, similar to the behavior observed in aqueous solutions. The increase of temperature above 110°C causes change of absorption spectra and shifts to 540 nm resulting in the color transition from blue to red. Reversible thermochromism was detected at the temperature up to 160°C. The absorption spectra shift to 500 nm in orange phase corresponding to the color transition changed from magenta-to-orange at the temperatures higher than 170°C. The color did not return to its natural blue at this stage. In the system of the microwave synthesis time, 15, 30 and 60 min exhibited the first color transition (blue to magenta) at ~120°C (Figure 7) and the color transition from magenta-to-orange at ~180°C. The poly(PCDA/ZnO) embedded PVA in microwave synthesis time of 15, 30 and 60 min exhibited color transition and reversibility higher than that of 5 min. This result indicated high molecular ordering within the assemblies after a long microwave synthesis time.

To elucidate the effective thermal stability, the thermal stability of poly(PCDA/ZnO) at different microwave synthesis times is examined. Poly(PCDA/ZnO) solutions undergo several heating/cooling cycles at 25°C and 90°C. At the temperature of 90°C, poly(PCDA/ZnO) turns purple color, however, upon cooling, it completely reverts back to its original blue color. The system of poly(PCDA/ZnO) embedded PVA yields consistent results about heating/cooling cycles at 25°C and 160°C. The color transition takes a few seconds. The reversible color transition can be repeated approximately 10 heating-cooling cycles, as seen in the %color plot (Figure 8(a-b). These results suggest that the poly(PCDA/ZnO) microwave-assisted exhibit thermal stability effectively.

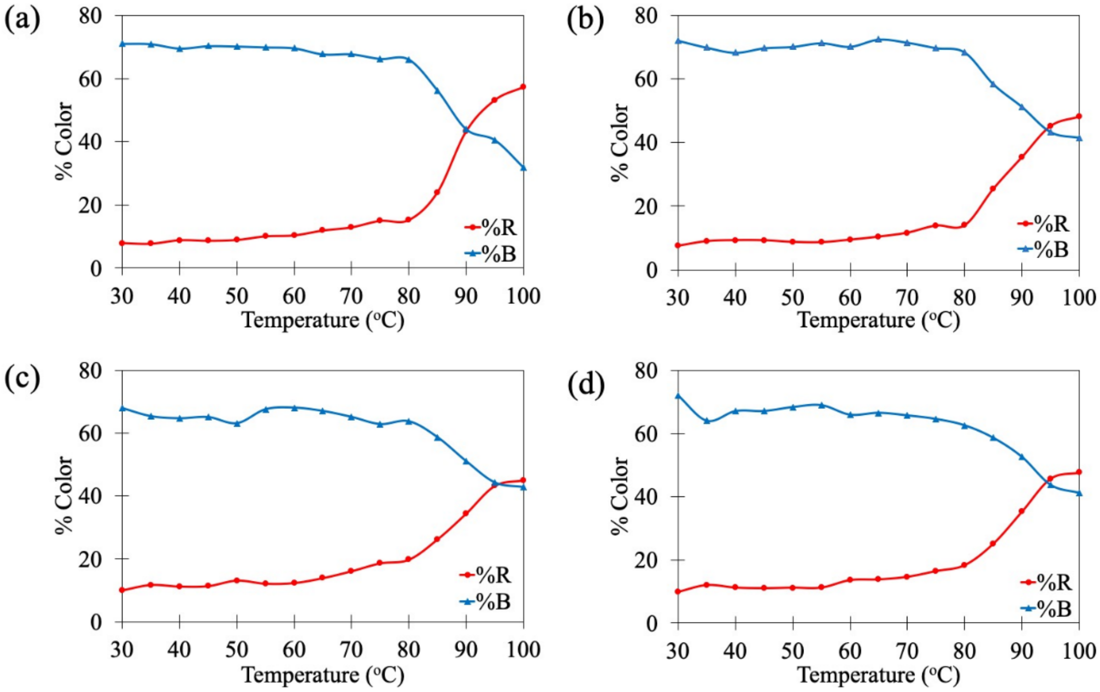

Figure 5. Plots of % color of poly(PCDA/ZnO) in aqueous suspension prepared by microwave-assisted technique with a microwave exposure time (a) 5, (b) 15, (c) 30, and (d) 60 min.

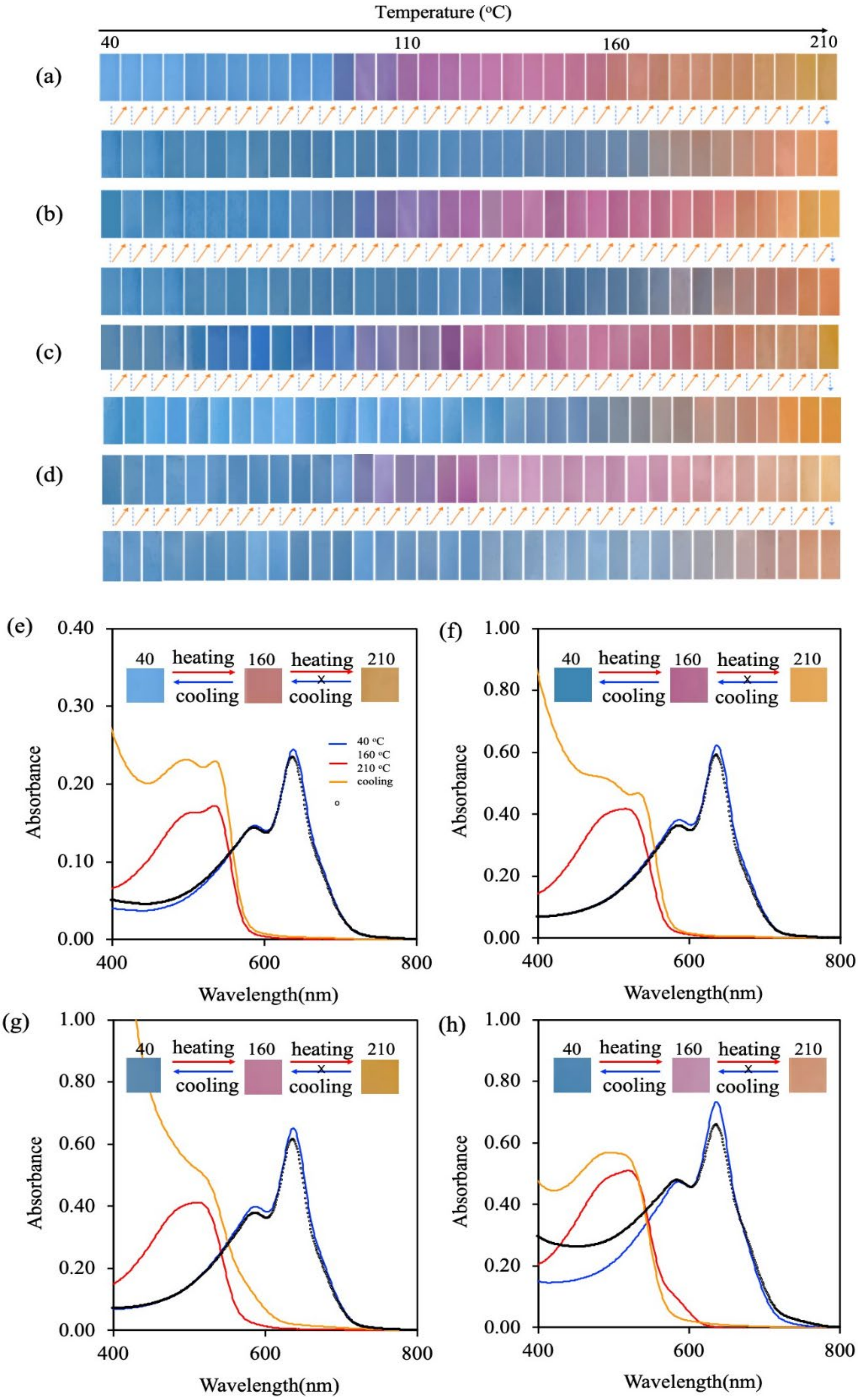

Figure 6. Color photographs and absorption spectra of poly(PCDA/ZnO) embed PVA prepared by microwave-assisted technique with a microwave exposure time of (a,e) 5, (b,f) 15, (c,g) 30 and (d,h) 60 minutes evaluated during the process of heating and cooling.

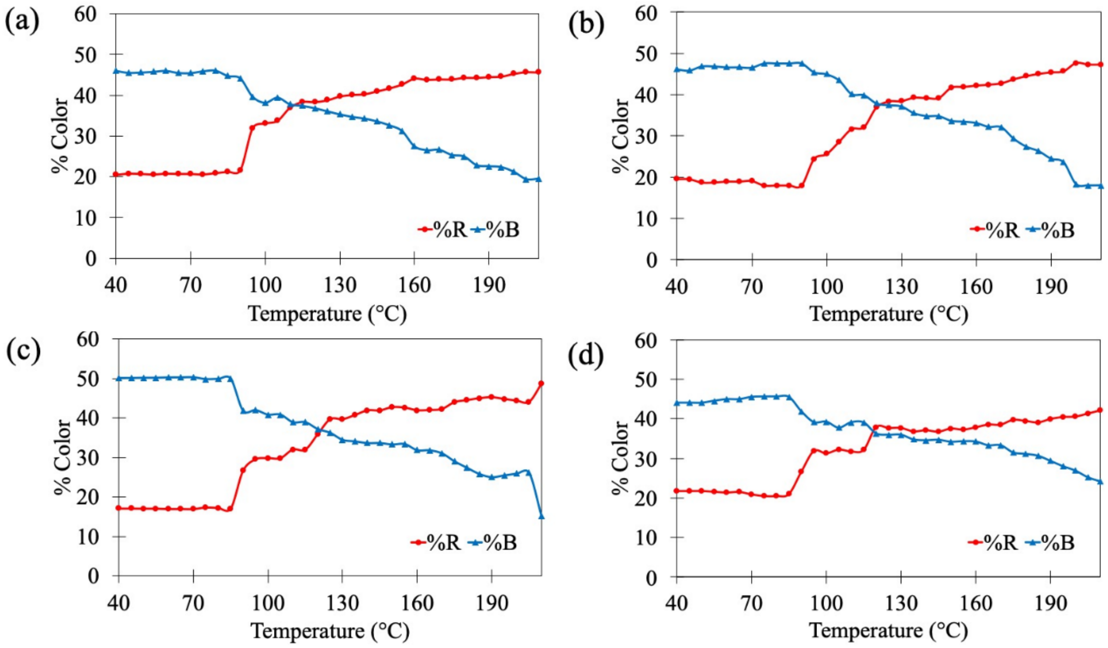

Figure 7. Plots of %color of poly(PCDA/ZnO) with PVA prepared by microwave-assisted technique with a microwave exposure time of (a) 5, (b) 15, (c) 30 and (d) 60 min.

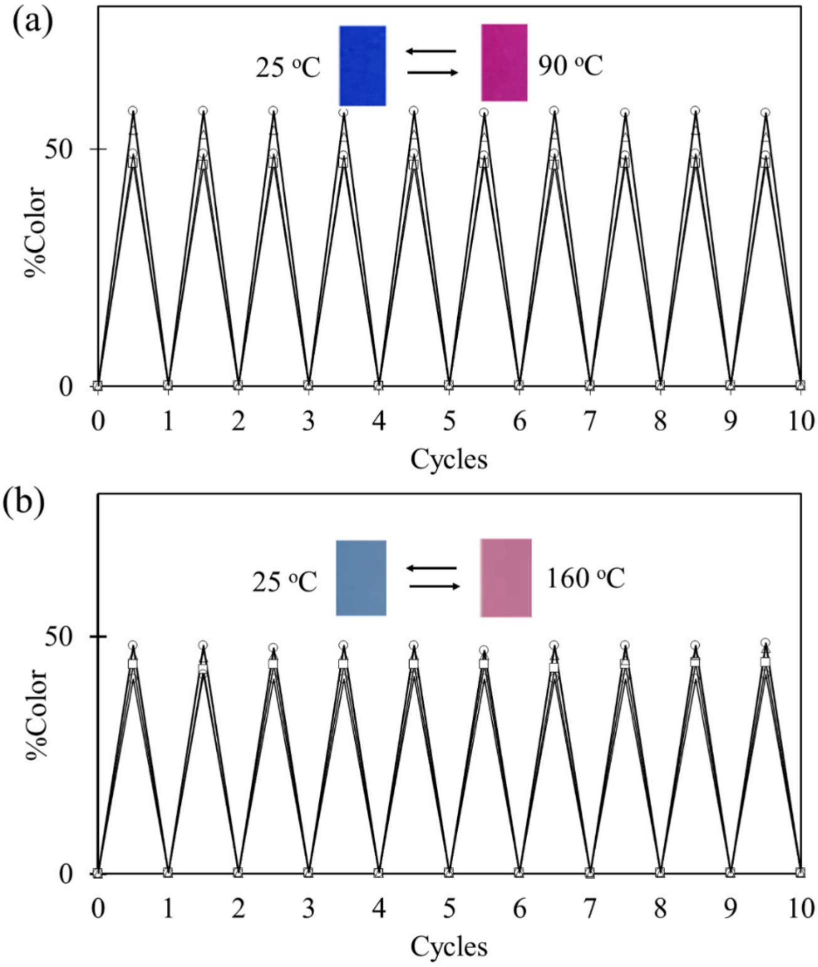

Figure 8. Change of % color during 10 heating–cooling cycles of poly(PCDA/ZnO) (a) solution and (b) embedded PVA. Symbols express microwave synthesis time for (○) 5 min, (Δ)15 min, (□) 30 min and (◊) 60 min.

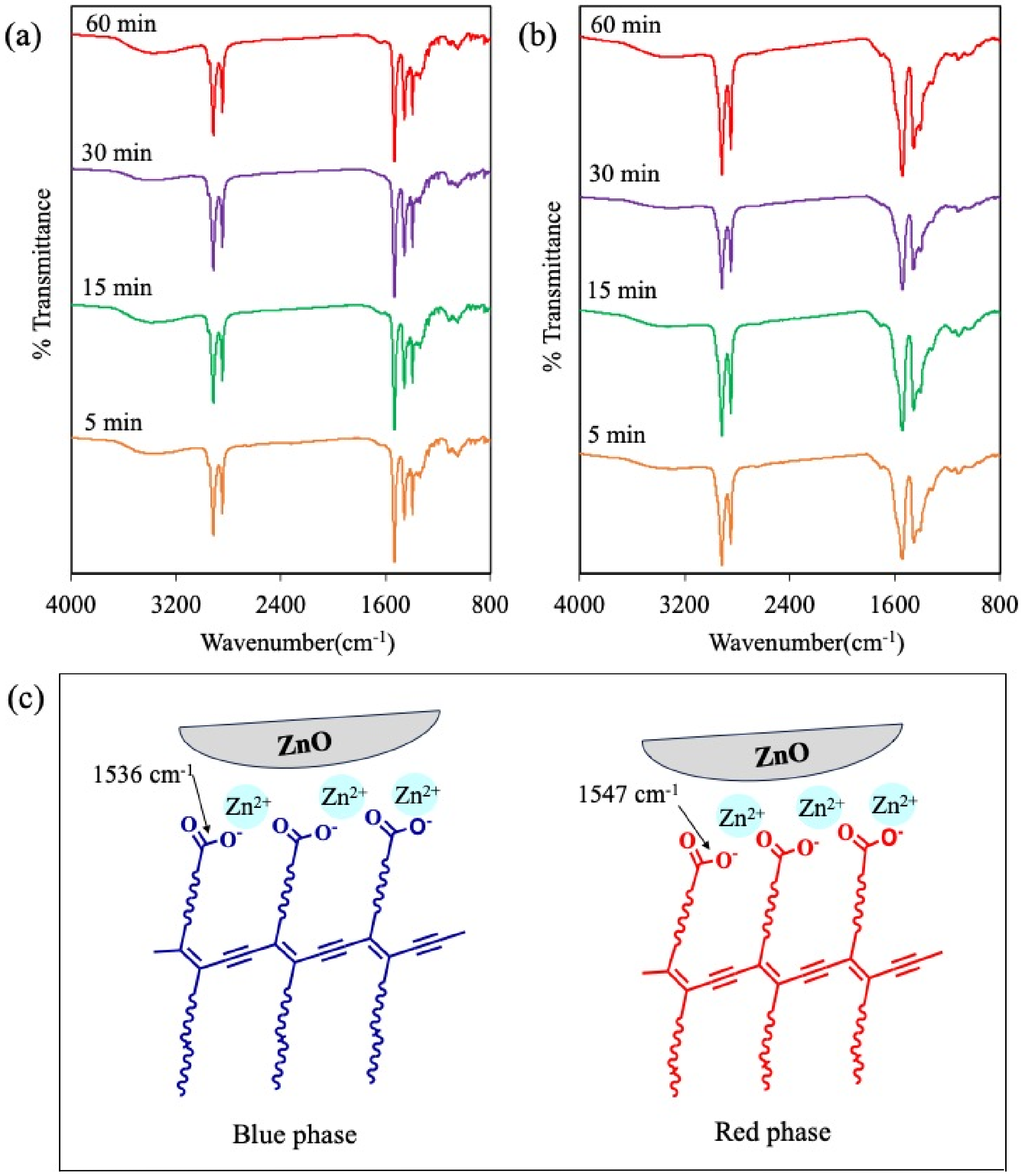

Figure 9. The comparison of FT-IR spectra of poly(PCDA/ZnO) in various microwave synthesis time of (a) the blue phase, (b) the red phase and (c) Vibrational numbers of -COO$^-$ group in blue phase and red phase.

IR spectroscopy was conducted to investigate the changes of local interactions in the poly(PCDA)/ZnO nanocomposite in which responsible for the irreversible color transition Figure 9 depicts the IR spectra of the drop-cast film of the nanocomposite in blue and red phases, which were examined from the same sample. During the drying process at room temperature, the ethanol molecule was removed from all samples. The transition from the blue to the red phase was obtained by annealing at 200°C for 5 min in an oven. The $\nu_s(CH_2)$ (2848 cm^{-1}) and $\nu_{as}(CH_2)$ (2916 cm^{-1}) of both phases were appeared at the same position, confirming that the alkyl side chains remained in an all-trans conformation during the transition. The asymmetric ν_{as}(COO) (1536 cm^{-1}) and ν_s(COO) (1395 cm^{-1}) stretching vibration of carboxylate anion shift to a higher wavenumber at 1547 cm^{-1} (ν_{as}(COO)) and 1408 cm^{-1} (ν_s(COO)). According to the findings, there was a partial rearrangement of the carboxylate anion at the ZnO surface during the irreversible transition. [22,45]. We propose the possible structure of carboxylate headgroups which interact with Zn^{2+} on the ZnO surface in both of blue phase and red phase of poly(PCDA/ZnO), corresponding to the asymmetric ν_{as}(COO$^-$) (1536 cm^{-1}) as shown in FT-IR spectra-(Figure 9(c)).

4. Conclusions

We demonstrate a new approach for the preparing poly(PCDA/ZnO) for controlling the thermochromic behaviors of PDA-based materials. The poly(PCDA/ZnO) prepared by microwave-assisted technique results in strong interfacial interactions and an increase in molecular ordering which affects morphology, particle size and thermochromic behaviors. The resultant poly(PCDA/ZnO) at high microwave synthesis time exhibits reversible thermochromism and high thermal stability. The poly(PCDA-ZnO) nanocomposite demonstrated high activity as a sensor for color transition temperature detection and reversible thermochromic detection, together with a considerable increase in detection time. The improved nanocomposite sensor can be attributed to the well-defined hexagonal sheet structure, which impacts strong molecular ordering within the assemblies. This finding may open up an attractive route for the synthesis of PDA-based materials for extensive application.

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